

Heat Capacity and Thermodynamic Properties of Beryllium 1:3-Aluminate, $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$, from 15 to 390 °K

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The heat capacity of beryllium 1:3-aluminate, $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$, was determined from 15 to 380 °K and the thermodynamic properties calculated from 0 to 390 °K. The entropy at 298.15 °K was found to be $175.55 \text{ J deg}^{-1} \text{ mol}^{-1}$ ($41.96 \text{ cal deg}^{-1} \text{ mol}^{-1}$).

Key Words: Beryllium 1:3-aluminate, enthalpy, entropy, Gibbs energy, heat capacity, low temperature calorimetry, thermodynamic properties.

1. Introduction

The results of the heat-capacity measurements on beryllium 1:3-aluminate,² $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$, from 15 to 380 °K presented herein have been obtained as a part of the program at the National Bureau of Standards to provide accurate thermodynamic data on “light-element” compounds. Earlier measurements on the $\text{BeO}-\text{Al}_2\text{O}_3$ system that have been reported from this laboratory are aluminum oxide (corundum), Al_2O_3 [3],³ and beryllium 1:1-aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$ [6]. Measurements on beryllium oxide, BeO , of relatively small crystal size have recently been completed [4] and will be reported in a future paper.

2. Sample

Lang et al. [9], reported “practically all $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ ” and “all $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ ” for the results of petrographic and x-ray examinations, respectively, on a sample prepared by fusing a mixture of 1 to 3 molal ratio of BeO to Al_2O_3 . Semi-Elements, Inc. prepared, on request, the sample accordingly for the heat-capacity measurements presented. The preparation procedure was as follows: stoichiometric amounts of dried BeO and Al_2O_3 powder were thoroughly mixed and fused in an arc furnace. To avoid contamination a fused mass was formed within a relatively large charge of the mixture so that the unfused mixture

would serve as the container for the fused portion of the material. The fused material was cooled to room temperature in about three hours, freed of any unfused material, and crushed and sieved to collect particle sizes between 0.3 and 2 mm (10 and 50 mesh) on the edge.

Some of the particles in the sample that was received appeared gray, presumably from occlusion of traces of carbon from the graphite electrodes used in the arc fusion preparation. Qualitative spectrochemical analysis of the material by the Spectrochemical Analysis Section of the National Bureau of Standards showed the limits of impurities given in table 1.

TABLE I. Spectrochemical analysis of beryllium 1:3-aluminate ($\text{BeO} \cdot 3\text{Al}_2\text{O}_3$)^a

Element	Percentage limit	Element	Percentage limit
Ag	< 0.0001	Mg	0.001–0.01
B	0.001–0.01	Mn	0.0001–0.001
Ca	0.001–0.01	Na	0.01–0.1
Cu	< 0.0001	Si	0.01–0.1
Fe	0.01–0.1	Zr	0.001–0.01

^a Analyzed by Elizabeth K. Hubbard, Spectrochemical Analysis Section.

A petrographic (microscopic) examination of the $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ sample was made in the Crystallography Section of the National Bureau of Standards. The crystal size was found to be on the average about 300μ .

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²The numbers indicate base to acid anhydride ratio.

³Figures in brackets indicate references listed at the end of this paper.

Since the sample was ground for the microscopic examination, the crystal size of the original 10 to 50 mesh polycrystalline material on which the heat-capacity measurements were made is considered to be larger than 300μ . The crystals were clear with some voids and growth defects resulting probably from too rapid cooling. There was some evidence of another phase being present, possibly up to about 5 percent. No BeO phase was detected.

X-ray diffraction examination of the $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ sample was also made in the Crystallography Section of the NBS. The pattern obtained is in agreement with published values for $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ [1, 2, 7] with some possible impurity lines close to $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ but without presence of all strong lines of these substances. A few unidentified lines were also found. The patterns corresponding to graphite, BeO, and $3\text{BeO} \cdot \text{Al}_2\text{O}_3$ were absent.

Optical properties of $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ have been found to be very similar [2, 7, 9, 10]. It seems, therefore, that the impurity phase observed petrographically in the sample investigated is probably not $\text{BeO} \cdot \text{Al}_2\text{O}_3$. If the undetectable $\text{BeO} \cdot \text{Al}_2\text{O}_3$ is present, then the excess Al_2O_3 should be observed as $\alpha\text{-Al}_2\text{O}_3$ or there is an unidentified compound of BeO and Al_2O_3 of ratio greater than 1 to 3. The x-ray pattern obtained does not definitively indicate the presence of $\alpha\text{-Al}_2\text{O}_3$.

Distinctive x-ray diffraction patterns have been reported for $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ [1, 2, 7]. Lang et al. [9], observed an unidentified phase of high refractive index in mixtures that have been heated to melting temperatures, having compositions between $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 . These investigators also found another unidentified phase in x-ray diffraction patterns of fused mixtures of composition between $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and BeO. The major *d*-spacings observed for the latter impurity phase cannot be identified with the *d* values reported for the more recently found $3\text{BeO} \cdot \text{Al}_2\text{O}_3$ phase [7]. Lang et al. [9], could not determine the presence of both of the unidentified phases in the same specimen or any similarity, if any, in the phases. They were not able to identify either phase in the same specimen by both petrographic and x-ray methods. These results seem to indicate that yet unidentified phases exist in the BeO— Al_2O_3 system or additional careful study of the known phases is needed.

Young [13] observed from x-ray measurements some disproportionation of $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ to $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 after heating for two weeks at 1150°C . This suggests that $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ is metastable in the range of the heat-capacity measurements obtained. Earlier, Foster and Royal [2] found $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ to have a stronger tendency toward crystal growth than $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and found no evidence for $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ to disproportionate. The relatively rapid cooling during the preparation of the sample used in the measurements presented here has apparently preserved the material mostly, if not all, in the $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ phase.

Chemical analysis of the $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ sample was performed in the Analysis and Purification Section of the NBS. Two 0.5 g samples were dissolved in hydro-

chloric acid by heating the mixture sealed in tubes at 250°C for 16 hr. The treatment of the resulting solution and the analysis for Be and Al were essentially the same as those described for $\text{BeO} \cdot \text{Al}_2\text{O}_3$ [6]. The results of the chemical analysis, summarized in table 2, show the beryllium and aluminum composition to have the theoretical stoichiometric ratio within the precision of the analytical method. The amount of graphite impurity was considered insignificant, and the sample was taken to be 100 percent $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ in the processing of the heat-capacity data obtained.

TABLE 2. *Chemical analysis of beryllium 1:3-aluminate ($\text{BeO} \cdot 3\text{Al}_2\text{O}_3$)*

Sample	Percentage by weight ^a		Mol ratio $\text{Al}_2\text{O}_3/\text{BeO}$
	Al	Be	
1	48.96	^b 2.71	3.017
2	48.93	^b 2.74	2.984
Theoretical	48.92	2.72	3.004

^a Analysis by E. J. Maienthal, Analysis and Purification Section.

^b Duplicate aliquots.

Although $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ is considered to be inert, the sample was handled and poured into the calorimeter vessel in a controlled-atmosphere box containing dry argon gas (dew-point of about -80°C). The calorimeter vessel was provided with a screw-cap and gasket closure and a "pump out" tube with a valve previously described [5]. The vessel containing the sample was pumped to a high vacuum and purged with dry helium gas several times and finally sealed with 60.5 torr pressure of helium gas. The mass of sample investigated was 252.1429 g.

3. Apparatus and Method

The heat-capacity measurements on $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ were made in an adiabatic calorimeter similar in principle and design to that described previously [11]. The calorimeter, sample container, and the adjuvant instruments were the same, except for the bridge, as those used for the recently published measurements on $\text{BeO} \cdot \text{Al}_2\text{O}_3$ [6]. Description of methods and procedures used for the measurements of temperature, power, and time interval of heating, and the calibration information on the temperature scale and electrical instruments are given in the reference.

An automatic Mueller bridge, capable of resistance measurements up to almost 500Ω to the nearest 0.00001 Ω , was used with the platinum-resistance thermometer for most of the temperature measurements. The performance of this automatic bridge was found comparable to the high-precision manually

operated Mueller bridge used exclusively in the measurements with $\text{BeO} \cdot \text{Al}_2\text{O}_3$ [6]. The bridge readings were automatically recorded on punch cards and subsequently processed on the high-speed digital computer to obtain the temperatures associated with each heating interval.

The 1961 atomic weights based on carbon 12 were used for converting the mass of sample investigated to gram formula weight basis [8]. The energy measurements were made in terms of the MKSA unit of energy, the joule. Wherever conversion to calorie was made, the following relation was used:

$$1 \text{ defined calorie} = 4.1840 \text{ J.}$$

4. Heat-Capacity Measurements and Results

Measurements totaling 147 heat-capacity "points" were obtained on the calorimeter vessel plus sample from about 15 to 390 °K and 87 points were obtained subsequently on the empty vessel in the same temperature range. Smoothed values of heat capacity at closely and regularly spaced integral temperatures were calculated for the two series of measurements using high-speed digital computer methods. The heat capacity of the sample was then obtained by differencing the smoothed values from the two series of measurements at the corresponding regular temperatures. The values of heat capacity for the $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ below 15 °K were obtained by extrapolating the smoothed experimental values at the lower temperatures in accordance with a T^3 relation.

Briefly, the procedures used in analyzing the experimental observations were as follows. Since the data could not be adequately represented over the complete temperature range in terms of a single heat-capacity equation, a number of polynomials of varying degrees of complexity were fitted by the method of least squares to the data over different temperature ranges. To avoid curvature corrections the analysis was formulated according to the relation:

$$Q_{T_2, T_1} = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C(T) dT,$$

where Q_{T_2, T_1} is the input energy, T_1 and T_2 the corresponding initial and final temperatures, respectively, for each of the points, and $C(T)$ is the polynomial for which the coefficients were obtained by the least-squares method. Three or four polynomials were selected from the group on the basis of their fit over the complete temperature range of observations and for their agreement where the temperatures overlap. The polynomials were evaluated at closely spaced regular temperatures and joined at temperatures where

the values of heat capacity and their first and second derivatives showed the best agreement. A numerical smoothing analysis was performed on these tabular values using the computer to test the smoothness of the joining process. Since the values were adequately smooth, they were changed insignificantly by the computer smoothing program.

The deviations of the observed values of heat capacity for the calorimeter-vessel-plus-sample and for the empty-vessel measurements from the final smoothed tabular values for the two series of measurements are plotted in figures 1 and 2, respectively. Except below about 50 °K, all of the observations are well within the ± 0.1 percent limit of the net heat capacity of the $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ sample.

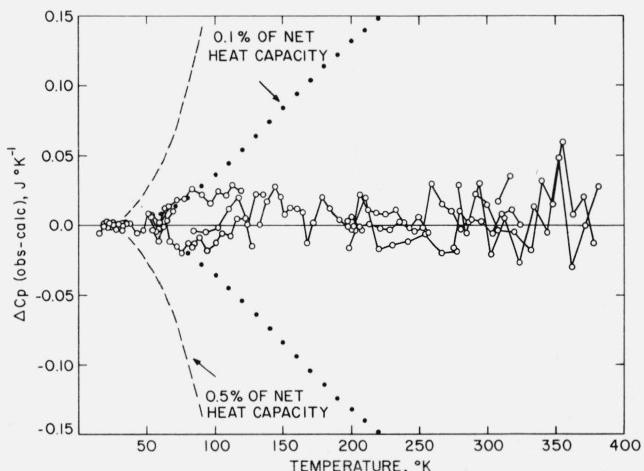


FIGURE 1. Deviations of the heat-capacity measurements on calorimeter vessel plus beryllium 1:3-aluminate, $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$.

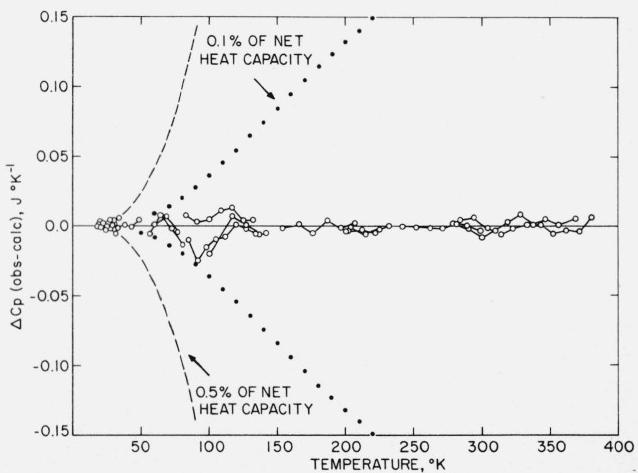


FIGURE 2. Deviations of the heat-capacity measurements on the empty calorimeter vessel used with beryllium 1:3-aluminate, $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$.

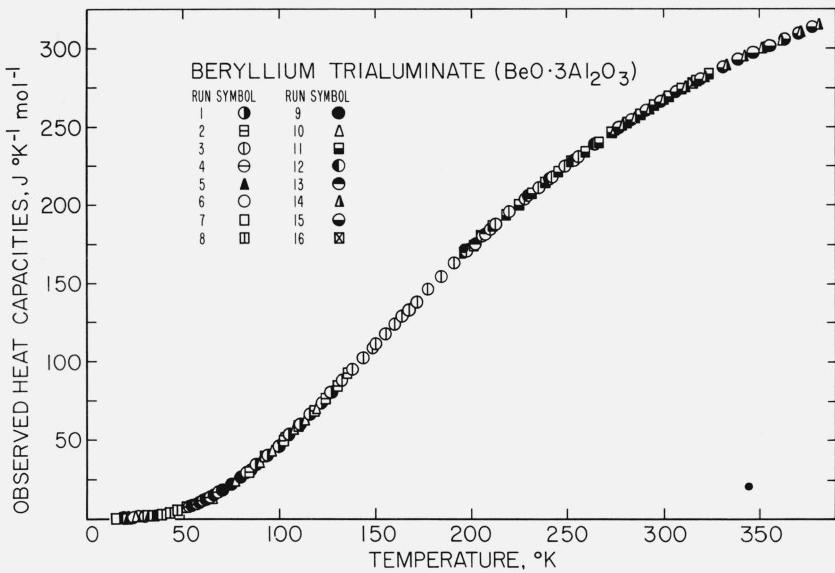


FIGURE 3. *Observed values of the molal heat capacity of beryllium 1:3-aluminate, BeO · 3Al₂O₃, as a function of the temperature.*
(Numerical values are given in table 3.)

The "observed molal heat capacity" is shown in figure 3 and listed in table 3 in the chronological order of the measurements made. These values were obtained by subtracting the smoothed heat capacity of the empty vessel from that of the calorimeter vessel plus sample at the observed temperatures (mid-temperatures of the heating intervals). The heat-capacity values of the empty vessel at the corresponding observed temperatures were obtained by interpolation in the table of smoothed values described earlier. Corrections were made for the heat capacity of helium gas and for curvature wherever significant and the net heat capacity converted to the molal observed values.

The final smoothed values of heat capacity of BeO · 3Al₂O₃ given in table 4 were obtained, however, by differencing at corresponding temperatures the smoothed values described earlier for the two series of measurements and correcting for the contribution of the helium exchange gas wherever significant. The smoothness of the resulting tabular values was checked on the computer and converted to molal values.

The smoothed values at the lower temperatures were plotted as C/T versus T^2 and extrapolated linearly to 0 °K to obtain values below 15 °K, the lower temperature limit of the experimental measurements. The slope of the line used was $4.025 \times 10^{-5} \text{ J deg}^{-4} \text{ mol}^{-1}$, which corresponds to an effective Debye characteristic temperature of 936 °K (assuming $C_V = C_p$).

5. Reliability of the Results

In addition to the imprecision of the measurements shown in figures 1 and 2, the purity of the sample, the accuracy of calibration of the instruments used, and the possible sources of systematic errors were examined to estimate the uncertainties in the final values of heat capacity of BeO · 3Al₂O₃. The estimated uncertainty in the values given in table 4 between 80 and 390 °K is ± 0.1 percent. Below about 80 °K, the uncertainty increased, because of the decrease in the contribution of the sample to the gross heat capacity. At 300 °K the heat capacity of the sample was 81 percent of the gross; at 80 °K, 46 percent; at 50 °K, 29 percent; 20 °K, 14 percent; and at 13 °K, only 10 percent. In addition, the sensitivity dR/dT of the platinum resistance thermometer began to decrease significantly below about 40 °K. Considering these factors, the estimated uncertainty is ± 0.2 percent at 50 °K, ± 1 percent at 20 °K, and ± 3 percent at 13 °K.

6. Thermodynamic Functions and Discussion of the Results

The thermodynamic functions for BeO · 3Al₂O₃ were derived, using their usual relations with respect to heat capacity, from the smoothed tabular values. The thermodynamic relations were evaluated on the com-

TABLE 3. Observed heat capacity of beryllium 1:3-aluminate
(BeO · 3Al₂O₃)

Gram molecular wt = 330.8952 g		1 cal = 4.1840 J		T °K = 273.15 + t °C	
T	C _p	T	C _p	T	C _p
RUN 1		RUN 6—Con.		RUN 11—Con.	
°K	J/deg-mol	°K	J/deg-mol	°K	J/deg-mol
82.8203	28.964	23.3504	0.532	295.3757	263.122
88.0822	34.227	26.8876	0.827	302.7188	268.501
93.6560	40.027	30.7964	1.270	309.9404	273.633
99.4640	46.435			317.0493	278.493
105.1819	53.076			324.0556	283.101
110.8937	59.946	RUN 7			
116.2799	66.639	14.7135	0.107		
121.5671	73.341	19.0305	0.279		
126.9319	80.234	21.4966	0.414	199.6885	172.558
		24.9047	0.654	209.5623	183.776
		28.9755	1.047	220.4510	195.579
				230.4099	205.954
				241.5414	217.011
				253.8218	228.599
				265.6168	239.092
				277.0019	248.759
		RUN 8			
		25.6653	0.718	198.0565	170.655
		29.7872	1.147	201.9686	175.189
		33.8800	1.737	207.2721	181.202
		38.4138	2.618		
		42.7876	3.715		
		46.9192	5.045		
		51.3870	6.817		
		56.0607	9.017		
		RUN 9			
		53.0258	7.546	275.0636	247.116
		57.5249	9.794	278.9339	250.319
		61.8323	12.339	285.8983	255.860
		66.0923	15.097	293.6534	261.865
		70.4018	18.206	301.7499	267.778
		74.9699	21.849	311.7800	274.892
		79.9109	26.210	322.8485	282.271
		85.1544	31.264	333.3522	288.997
				343.2091	294.909
				352.1076	300.070
		RUN 10			
		53.4833	7.764	361.4226	305.043
		58.9604	10.617	371.2744	310.239
		64.5559	14.102	380.9849	315.212
		70.6195	18.435		
		77.0761	23.717		
		83.3997	29.590		
		89.8264	36.063		
		96.1066	42.727		
		102.1024	49.512		
		107.8188	56.257		
		113.3406	63.011		
		119.0752	70.194		
		RUN 11			
		196.3894	168.737	277.8938	249.497
		200.5662	173.578	284.1183	254.451
		206.1477	179.973	290.9840	259.825
		212.0283	186.512	298.9705	265.799
		218.3673	193.399	307.2420	271.725
		224.7804	200.188	319.3254	279.963
		231.5555	207.161	331.2745	287.670
		238.6756	214.253	339.1056	292.530
		245.6172	220.957	346.9111	297.086
		252.3915	227.307	354.6113	301.477
		259.3612	233.673	362.3108	305.570
		266.5257	239.939	369.8374	309.529
		273.6103	246.048	377.2870	313.293
		RUN 12			
		18.4505	0.250	199.6885	172.558
		21.0068	0.381	207.2721	181.202

TABLE 4. Thermodynamic functions for beryllium 1:3-aluminate
(BeO · 3Al₂O₃) solid phase.

Gram molecular wt = 330.8952 g		1 cal = 4.1840 J		T °K = 273.15 + t °C	
T	C _p ⁰	(H _T ⁰ - H ₀ ⁰)	(H _T ⁰ - H ₀ ⁰) / T	(S _T - S ₀ ⁰)	-(G _T ⁰ - G ₀ ⁰)
°K	J/deg-mol	J/mol	J/deg-mol	J/mol	J/deg-mol
0.00	0.000	0.000	0.000	0.000	0.000
5.00	0.005	0.006	0.001	0.002	0.002
10.00	0.040	0.101	0.010	0.013	0.034
15.00	0.135	0.509	0.034	0.045	0.170
20.00	0.326	1.611	0.081	0.107	0.536
25.00	0.656	4.002	0.160	0.213	1.316
30.00	1.167	8.470	0.282	0.374	2.757
35.00	1.919	16.072	0.459	0.607	5.177
40.00	2.973	28.165	0.704	0.928	9.875
45.00	4.387	46.405	1.031	1.357	14.639
50.00	6.208	72.717	1.454	1.909	22.748
80.00	26.294	521.98	6.525	8.583	164.68
85.00	31.114	665.35	7.828	10.320	211.86
90.00	36.197	833.56	9.262	12.242	268.19
95.00	41.483	1027.7	10.817	14.339	334.57
100.00	47.050	1248.9	12.489	16.607	411.87
130.00	84.236	3205.8	24.660	33.508	1150.3
135.00	90.790	3643.3	26.987	36.810	1326.0
140.00	97.375	4113.7	29.384	40.230	1518.6
145.00	103.97	4617.1	31.842	43.763	1728.5
150.00	110.55	5153.4	34.356	47.398	1956.4
155.00	117.11	5722.5	36.920	51.130	2202.6
160.00	123.62	6324.4	39.527	54.951	2467.8
165.00	130.07	6958.6	42.173	58.854	2752.3
170.00	136.46	7625.0	44.853	62.832	3056.5
175.00	142.77	8323.1	47.560	66.879	3380.7
180.00	148.99	9052.5	50.292	70.988	3725.4
185.00	155.13	9812.9	53.042	75.154	4090.7
190.00	161.16	10604.	55.808	79.372	4477.0
195.00	167.10	11424.	58.586	83.635	4884.5
200.00	172.93	12274.	61.372	87.939	5313.4
205.00	178.65	13153.	64.163	92.280	5763.9
210.00	184.26	14061.	66.956	96.652	6236.3
215.00	189.75	14996.	69.748	101.05	73.035
220.00	195.14	15958.	72.536	105.48	7246.8
225.00	200.41	16947.	75.320	109.92	7785.3
230.00	205.57	17962.	78.095	114.38	8346.1
235.00	210.62	19002.	80.862	118.86	8929.2
240.00	215.56	20068.	83.616	123.34	9534.7
245.00	220.38	21158.	86.359	127.84	10163.
250.00	225.10	22272.	89.086	132.34	10813.
255.00	229.71	23409.	91.799	136.84	11486.
260.00	234.21	24568.	94.494	141.35	12181.
265.00	238.61	25751.	97.172	145.85	12899.
270.00	242.90	26954.	99.831	150.35	13640.
275.15	245.55	27724.	101.50	153.18	14118.
275.00	247.09	28179.	102.47	154.84	14403.
280.00	251.17	29425.	105.09	159.33	15188.
285.00	255.16	30691.	107.69	163.81	15996.
290.00	259.05	31977.	110.26	168.29	16827.
295.00	262.84	32381.	112.82	172.75	17679.
298.15	265.19	34113.	114.42	175.55	18228.
300.00	266.54	34605.	115.35	177.20	18554.
305.00	270.15	35947.	117.86	181.63	19451.
310.00	273.67	37306.	120.34	186.05	20370.
315.00	277.11	38683.	122.80	190.46	21312.

TABLE 4. Thermodynamic functions for beryllium 1:3-aluminate
(BeO · 3Al₂O₃) solid phase.
Gram Molecular wt = 330.8952 g 1 cal = 4.1840 J
 $T^{\circ}\text{K} = 273.15 + t^{\circ}\text{C}$

T	C_p^0	$(H_r^0 - H_o^0)$	$(H_r^0 - H_o^0)/T$	$(S_r - S_o^0)$	$-(G_r^0 - H_o^0)$	$-(G_r^0 - H_o^0)/T$
°K	J/deg-mol	J/mol	J/deg-mol	J/deg-mol	J/mol	J/deg-mol
320.00	280.46	40077.	125.24	194.85	22275.	69.609
325.00	283.72	41488.	127.65	199.22	23260.	71.569
330.00	286.90	42914.	130.04	203.58	24267.	73.537
335.00	290.00	44356.	132.41	207.92	25296.	75.510
340.00	293.02	45814.	134.75	212.24	26346.	77.489
345.00	295.96	47287.	137.06	216.54	27418.	79.473
350.00	298.82	48774.	139.35	220.81	28512.	81.461
355.00	301.60	50275.	141.62	225.07	29626.	83.454
360.00	304.32	51789.	143.86	229.31	30762.	85.451
365.00	306.98	53318.	146.08	233.53	31919.	87.450
370.00	309.59	54859.	148.27	237.72	33097.	89.452
373.15	311.21	55837.	149.64	240.35	33850.	90.715
375.00	312.15	56413.	150.44	241.89	34296.	91.457
380.00	314.68	57981.	152.58	246.04	35516.	93.464
385.00	317.19	59560.	154.70	250.17	36757.	95.472
390.00	319.69	61152.	156.80	254.28	38018.	97.482

H_o^0 and S_o^0 apply to the reference state of the solid at zero °K.

puter by numerical integration procedures with four-point Lagrangian integration coefficients [12]. The thermodynamic functions are given in table 4 from 0 to 390 °K.

Although x-ray diffraction measurements on BeO · 3Al₂O₃ have been reported [1, 2, 7], no information on the crystal structure of the material has been found. The room temperature density (3.73 g cm⁻³ [2]) of BeO · 3Al₂O₃ indicates that the crystal is more loosely bound on the average than the parent oxides, BeO and Al₂O₃. The molal volume, $V(\text{BeO} \cdot 3\text{Al}_2\text{O}_3)$, of BeO · 3Al₂O₃ is larger (4.03%) than the sum of the molal volumes, $V(\text{BeO}) + 3V(\text{Al}_2\text{O}_3)$, of BeO and Al₂O₃, respectively. The molal volume of BeO · 3Al₂O₃ is also larger (3.56%) than the sum of the molal volumes, $V(\text{BeO} \cdot \text{Al}_2\text{O}_3) + 2V(\text{Al}_2\text{O}_3)$, of BeO · Al₂O₃ and Al₂O₃, respectively. The molal volume of BeO · Al₂O₃ is likewise larger (1.21%) than the volume of equimolar mixture of BeO and Al₂O₃.

A comparison (fig. 4) of the heat capacity of BeO · 3Al₂O₃ with those of the corresponding molar mixtures of BeO and Al₂O₃ and of BeO · Al₂O₃ and Al₂O₃ shows a positive deviation throughout the temperature range (15 to 390 °K), with the deviations increasing with decrease in temperature. A similar positive deviation from "additivity" of the heat capacity was found with BeO · Al₂O₃ [6] (fig. 4) and with many mixed metal oxides reported in the literature. Also, with the exception of a few, where the density data may possibly be in error, a positive deviation from the additivity of the molal volumes was found at room temperature for the same mixed metal oxides. For substances at temperatures below the classical heat capacity limit, this correspondence is reasonable since a more open structure yields a "softer" force constant and hence, a lower Debye characteristic temperature. Further comparison of heat capacity and volume over a wide range of temperature is in progress, but unfortunately

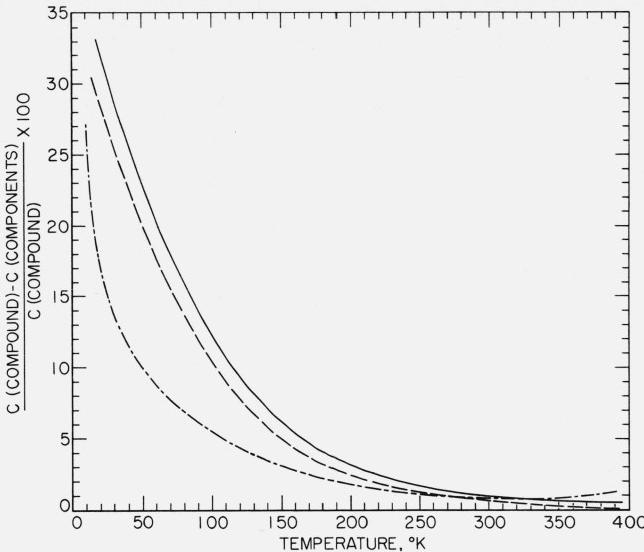


FIGURE 4. Comparison of the additivity of heat capacities:
— BeO · 3Al₂O₃ versus BeO + 3Al₂O₃
- - - BeO · 3Al₂O₃ versus BeO · Al₂O₃ + 2Al₂O₃
- - - - BeO · Al₂O₃ versus BeO + Al₂O₃

relatively few thermal expansion data seem to be available for the range below room temperature.

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7. References

- [1] P. P. Budnikov, V. G. Avetikov, E. I. Dudavsky, and A. A. Zvyagilsky, Doklady Akad. Nauk SSSR **68**, 313 (1949).
- [2] W. R. Foster and H. F. Royal, J. Am. Ceram. Soc. **32**, 26 (1949).
- [3] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Res. NBS **57**, 67 (1956) RP2694.
- [4] G. T. Furukawa and M. L. Reilly, unpublished measurements.
- [5] G. T. Furukawa, M. L. Reilly, and J. H. Picciarelli, J. Res. NBS **68A** (Phys. and Chem.) No. 4, 381 (1964).
- [6] G. T. Furukawa and W. G. Saba, J. Res. NBS **69A** (Phys. and Chem.) No. 1, 13 (1965).
- [7] F. Ya. Galakov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, No. 9, 1035 (1957); Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 9, 1062 (1957).
- [8] A. E. Cameron and E. Wichers, J. Am. Chem. Soc. **84**, 4192 (1962).
- [9] S. M. Lang, C. L. Fillmore, and L. H. Maxwell, J. Res. NBS **48**, 298 (1952) RP2316.
- [10] C. Palache, H. Berman, and C. Frondel, The System of Mineralogy, Vol. 1, p. 718 (J. Wiley & Sons, Inc., New York, N.Y., 1944).
- [11] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Res. NBS **35**, 39 (1945) RP1661.
- [12] Tables of Lagrangian Interpolation Coefficients (Columbia University Press, New York, N.Y., 1944).
- [13] W. A. Young, J. Phys. Chem. **64**, 1003 (1960).